FORMATION AND OPTICAL PROPERTIES OF PHOTOCHROMIC SILVER NANOPARTICLES

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April 4, 2005
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FORMATION AND OPTICAL PROPERTIES OF PHOTOCHROMIC SILVER NANOPARTICLES

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

By

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Fairbanks, Alaska

May 2005

Abstract

Spherical silver nanoparticles may be produced by the reduction of Ag^{+} (aq) by borohydride in the presences of citrate. When (phenylphosphinidene) bis-(benzenesulfonic acid) is also present, and the reaction mixture is illuminated, nonspherical Ag nanoparticles are formed. We have discovered that the shape of some Ag nanoparticles can be repeatedly changed by subjecting them to numerous cycles of light and dark. To our knowledge, this has never been reported in the literature. These photochromic Ag nanoparticles displayed at least two different particle shapes: prismatic and spherical. The difference in morphology could be determined by the color of the solution and by the electronic spectra. The prismatic Ag nanoparticles can be photochemically synthesized in 24hrs and then converted into a spherical form by placing them in the dark for 14hrs. This transformation is accompanied by a blue shift in the visible spectrum. The prismatic particles are reformed by placing them in the light for 4 hrs. This transformation has a red shift in the visible spectrum.

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Acknowledgements

I would like to thank my committee, Dr. Richard Stolzberg, Dr. Thomas Trainor, and Dr. William Howard for their contribution to the completion of my research and project. They helped me during every step of this project.

I would also like to thank my sister Mary R. Lee. She was there for me during the good times and the bad.

I would also like to thank my family. They have always been there for me. I never could have done this without you. I love you all.

Finally, I would like to thank the UAF chemistry department as a whole for all of the incredible support given to me.

Chapter 1.0

Introduction

A surge of interest in synthesizing colloidal silver nanoparticles emerged throughout the last decade, captivating the interest of many scientists. A wide range of shapes, [20] including spherical, [4] prismatic, [7, 14, 19, 21, 23, 30] cubes, [2, 27] rods [11, 15, 30] and plates [6, 16, 18] have been made. These different shaped Ag nanoparticles give a wide range of optical properties [8, 9, 10, 20] due to the unusually strong surface plasmon oscillation [3] of Ag. The wide range of optical properties suggest Ag nanoparticles may be useful as part of the transducer system of chemical sensors. Applications are especially likely in the areas involving biochemical sensors. [16, 17]

During our investigation, an interesting property of Ag nanoparticles was observed. These particles changed shape depending on light conditions. While in the dark, particle shapes were spherical. During illumination, particle shapes were prismatic. Our research efforts went into characterizing the formation and optical properties these photochromic silver nanoparticles

The three critical steps of seeding (reduction), [3] nucleation, [3] and growth [13, 25] accompany the synthesis of photochromic silver nanoparticles. Researchers reported significantly different results by a small change in the technique or protocol used to advance one of these critical steps. [1, 2, 7, 13, 26, 29]

The synthesis of Ag nanoparticles begins with the reduction Ag^+ (aq). Numerous chemical species have been used to reduce silver ions, including borohydride, [12, 14] ascorbate, [22] and poly (vinyl pyrrolidone) [28] using a reaction similar to (Equation 1).

$4\ Ag^{+}(aq) + BH_4^{-}(aq) + 3H_2O(l) \rightarrow 4\ Ag^{0}(s) + H_2BO_3^{-}(aq) + 4\ H^{+}(aq) + 2H_2(g)$ (1)

During reduction, subcolloidal Ag^{0} particles form via condensation reactions as short-lived intermediates [3, 13] of elemental Ag atoms into small aggregates (Equation 2).

$$Ag^{0} + Ag_n^{0} \rightarrow Ag_{n+1}^{0} \quad (2)$$

Stabilizers are used in metal nanoparticles synthesis to prevent agglomeration. The stabilizer allows the formation of an electric double layer at the surface of the nanoparticles. Nanoparticles with the same surface charge will not interact with one another because of coulombic repulsion. Citrate was used exclusively throughout this thesis as the initial stabilizer (Equation 3).

$$m\ Ag_n^{0}(s) + X\ citrate\ (aq) \rightarrow Ag_{n\,m}(citrate)_x\ (s) \quad (3)$$

If two stabilizers are present, a competetive equilibrium will occur (Equation 4). Within this thesis citrate and BSPP were used. The BSPP ion will displace some of the citrate ion on the surface of the Ag nanoparticle. Increasing the concentration of BSPP will cause a higher number of displaced citrate ions by BSPP ions (Equation 4).

$Ag_n(citrate)x\ (s) + z\ BSPP\ (aq) \rightarrow Ag_n(citrate)_{x-z}(BSPP)_z\ (s) + z\ citrate\ (aq)$ (4)

The nucleation of Ag in the presence of citrate forms spherical shaped nanoclusters, typically 20 nm in diameter. These are the particles that have been produced and studied extensively over the past decade.

Researchers have used optical illumination [1, 14, 20] during the growth step to increase particle size and transform the spherical clusters into a variety of nonspherical morphologies, including prismatic nanoparticles. [5, 7, 20] (4)

$$Ag_n\ (spherical) \xrightarrow{h\nu} Ag_m\ (prismatic) \quad (4)$$

The shape of the particle depends on the stabilizers, ratios of capping agents, [24] and wavelength of light.

The goal of this thesis is to give a detailed discussion about synthesis and characteristics of photochromic Ag nanoparticles. It will detail essential photochromic variables and photochromic limitations.

Chapter 2.0

Experimental Procedures and Method Development

2.1 Materials & Equipment

2.1.1 Reagents

Photochromic Ag nanoparticles were synthesized with silver nitrate (99.93%, Thorn Smith Laboratories), sodium citrate (reagent grade, Aldrich), sodium borohydride (reagent grade, Aldrich), and 4, 4-(phenylphosphinidene) bis-(benzenesulfonic acid) (BSPP) (reagent grade, Aldrich).

2.1.2 Solvents

Reverse osmosis water (18 MΩ-ohm DI-water) was used for the preparation of solutions.

2.1.3 Miscellaneous Materials

A fixture with two full spectrum fluorescent tubes (Philips F32T8/TL741 universal/hi-visible) was used in the synthesis of Ag nanoparticles. The emission spectrum is shown in Figure 1.

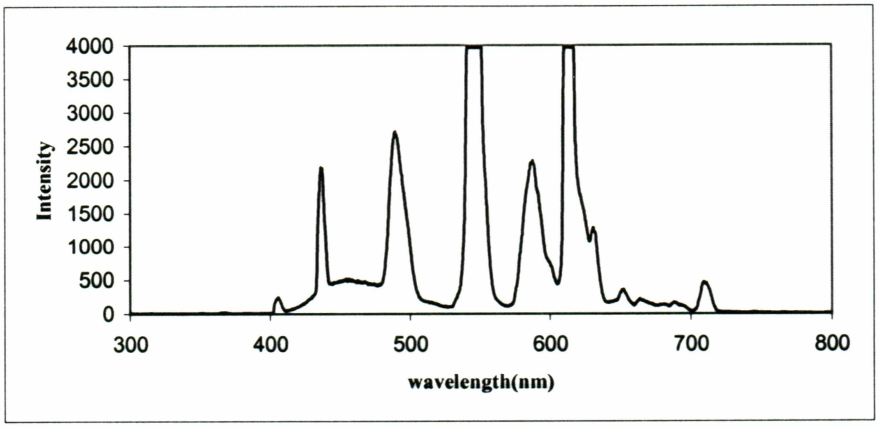

Figure 1: Philips F32T8 emission spectrum.

Four filters were used for the experiment detailed in section 2.3.3, these were Turner WG-305, GG-455, RG-610 and BG-24. The filtered emission spectrum of the Philips F32T8 lamps is shown in Figure 2 and absorption profile of the filters is shown in Figure 3.

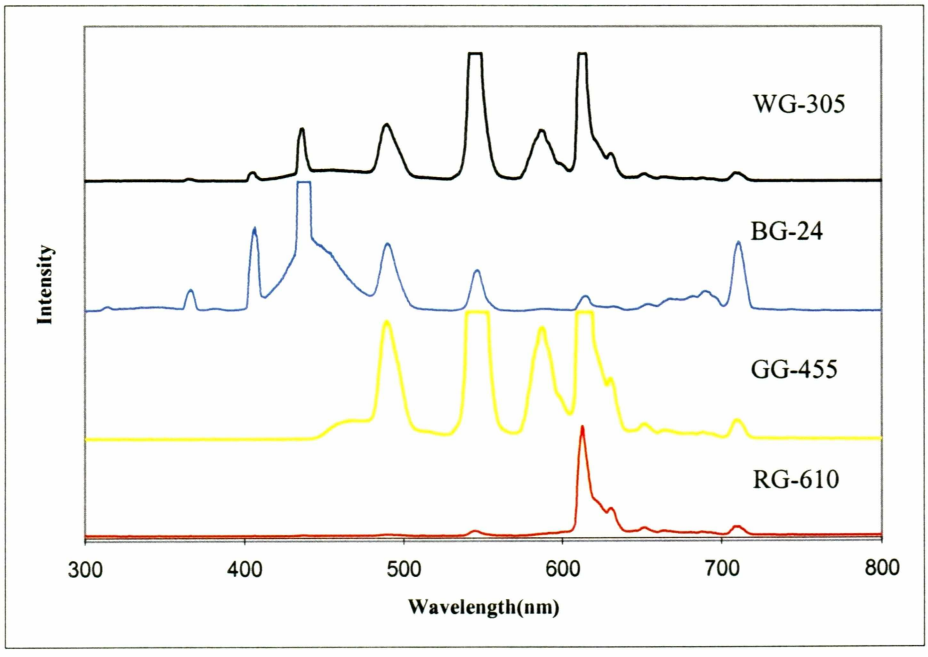

Figure 2: Emission spectra for Philips F32T8 Lamps after passing through WG-305, BG-24, GG-455, and RG-610 filters.

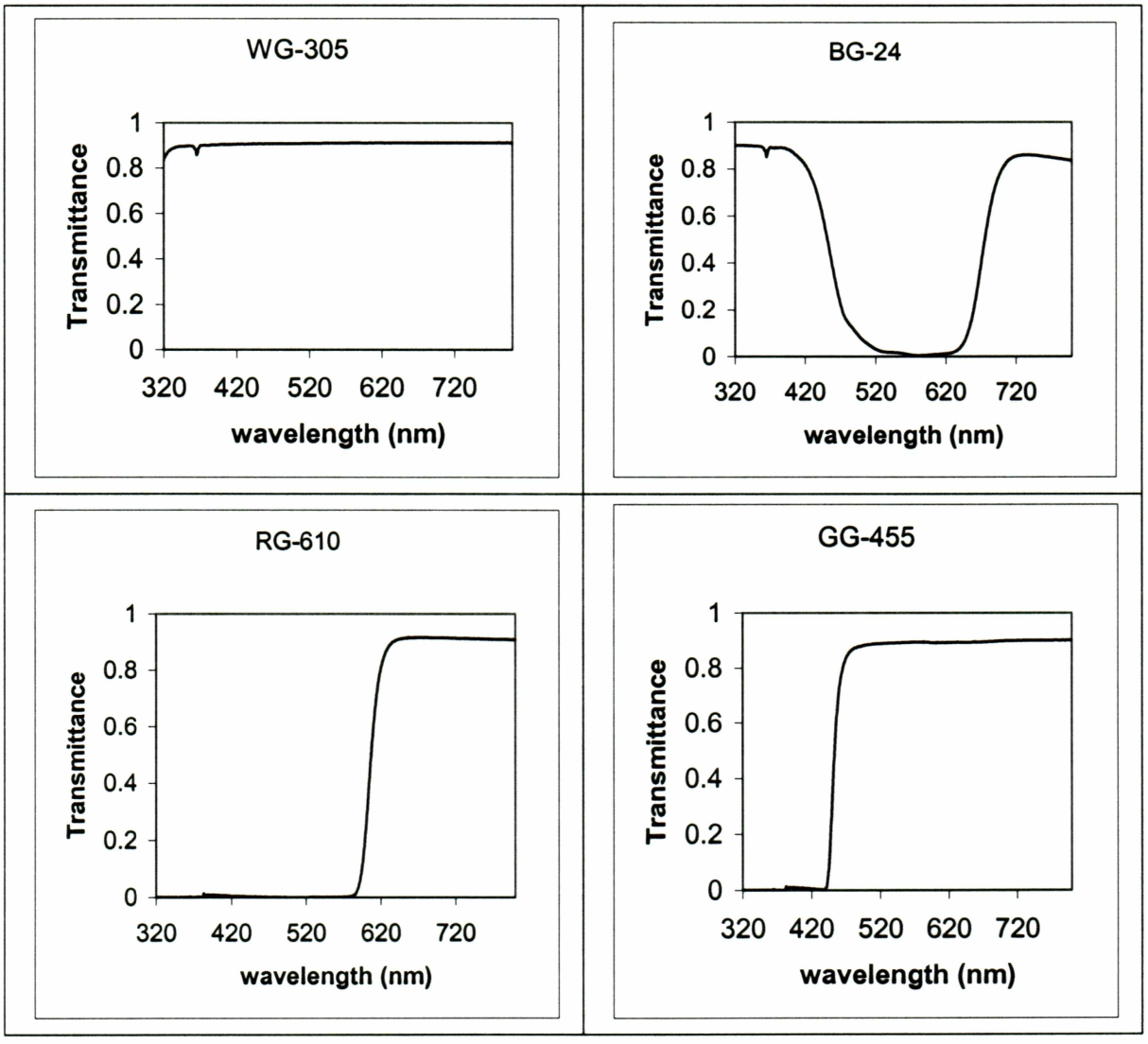

Figure 3: Transmission spectra of 4 filters.

2.1.4 Instruments

The Hewlett Packard model 8453A series was used for UV-visible data acquisition. The Zeta Potential Analyzer model 90Plus/BI-MAS dynamic light scattering were used for average particle sizing. The transmission electron microscope model Joel JEM-1200EX was used for particle imaging.

2.1.4.1 UV-Visible Data Acquisition

The UV-visible analysis was done by using 1 cm plastic cuvettes. Blanks were done with reverse osmosis water.

Kinetics runs were done by first centering the bulbs directly over the sample which was contained in a cuvette in the sample compartment of the HP8453A spectrometer. The first spectrum was obtained for dark form particles. The lights were turned on and spectra were acquired every 15 min for kinetic runs of 5 hrs or less, and every 1 hr for kinetic runs longer than 5 hrs. A polyvinylidene chloride (Saran wrap) cover was used to eliminate evaporation.

All UV-visible data were scrutinized to remove outliers before any data analysis was conducted. Some spectra were baseline corrected at 1000, 1050, or 1100 nm using a 3 point average (±1 nm from 1000, 1050, or 1100 nm). Offset data points caused by improperly functioning diodes were cleaned by averaging the prior data point intensity value with the post data point intensity value.

The analysis was done with the multivariate package Unscrambler (CAMO ASA, Oslo, Norway). The analysis involved ten variables: [Ag], [BH_4^+], [Cit], [BSPP], [Ag]/ [BH_4^+], [Ag]/ [Cit], [Ag]/ [BSPP], [BH_4^+]/ [Cit], [BH_4^+]/ [BSPP] and [Cit]/ [BSPP]. The wavelength shift values between dark and light form were used as a response. Model validation was done by leverage correction.

2.1.4.2 Particle Sizing

Particle size analysis was done by using 10mm, 4.5 ml, square, four sided, clear, polystyrene cuvettes. Data acquisition was done using ZetaPlus particle sizing software (Brookhaven Instrument Corporation). Maximized incident power was calibrated by using a supplied solution of 92 nm polystyrene spheres. The parameters for refractive index of particle variables were Real 1.590, Imaginary 0.000, and Dust Cutoff 80.00. Running parameters were refractive index 1.331, viscosity 0.955 cP, temperature 22 °C. The time variables depended on the experiment (see appropriate experiment). The irradiation source was a 657.0 nm laser. The cuvettes were covered with plastic caps for normal data acquisition or Saran wrap for kinetic runs.

Cuvettes containing dark form solutions were placed inside of the Zeta Potential Analyzer. Lamp bulbs were fixed approximately 8 inches directly above the sample holder of the instrument (Figure 4). The kinetic runs were done over a 5 hr time frame with data acquisition beginning at 0 s and gathered every 15 min. The temperature was set at 22 °C.

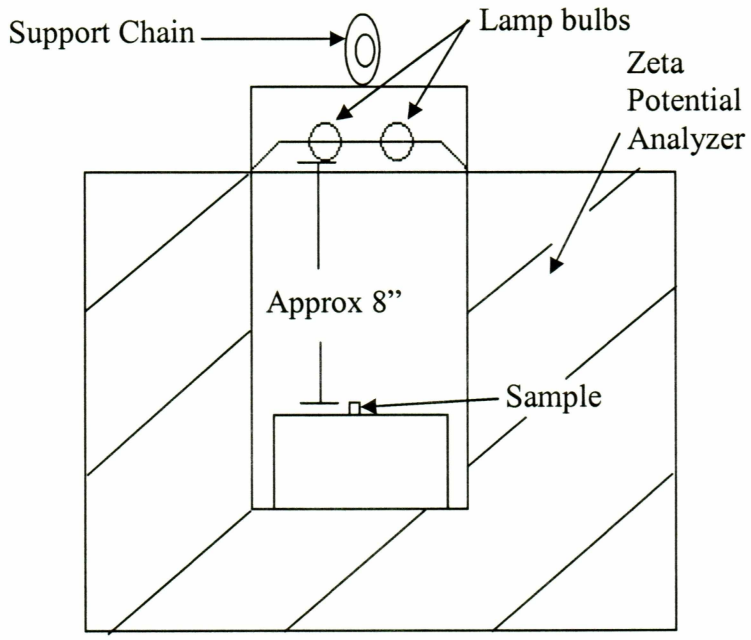

Figure 4: Lamp setup for Zeta potential analyzer experiment.

2.1.4.3 Transmission Electron Microscope Imaging

A transmission electron microscope was used for particle imaging. A precentered hairpin type tungsten filament was used. Instrument variables were standard magnification mode 150 - 200k X, acceleration voltage 70kV.

2.2 Sample Preparations

All glassware was rinsed once with RO water, once with 2M HNO_3 for 10 min, rinsed again with RO-water, and allowed to dry completely. All solutions were swirled as the reagents were added from stock solutions to ensure proper homogenization. In preliminary studies large shifts occurred most frequently with concentrations of 50 μM Ag^+, 200 μM citrate, 200 μM BH_4^-, and 50 μM BSPP. As a result, all subsequent experiments were conducted within this range of values. All experiments were done with the full spectrum bulbs and BSPP added last (see 2.3.1 for further details). Unless otherwise stated in the following individual sections, photochromic particles were prepared by six steps.

1. Solutions of 50 μM Ag^+ were prepared by dilution of 0.01M $AgNO_3$ stock solution.
2. Sodium citrate was added to the desired concentration of 200 μM.
3. Reduction of Ag^+ was done by addition of $NaBH_4$ at a concentration of 200 μM.
4. BSPP was added to a concentration of 50 μM.
5. The solutions were all placed approximately 4 inches under the bulbs (center of bulb to top of solution) for 24 hrs where a blue color would develop (photodeveloped form).
6. The solutions were placed in the dark for 24 hrs. During this time the solutions would change to a red color (dark form). If the dark form solutions were illuminated for 5 hrs the solutions would change from red to a blue color (light form).

2.3 Experimental Protocols

2.3.1 Testing the Importance of Addition Order for Photochromic Development

An obvious question arose early in the investigation of the photochromic particles. Why would solutions (with the same chemical composition) change color when placed in the dark, while others did not display this tendency at all? An investigation by Joshua Klynstra tested the importance of addition order for the reagents. He has consented for his observations to be used in this thesis.

Regarding the order of addition, *BSPP First* refers to when Ag^+ was reduced in the presence of BSPP (Equation 5) and *BSPP Last* refers to when Ag^+ was reduced in the absence of the BSPP (Equation 6).

$$n\,Ag^+ \xrightarrow[3)\ BH_4^-]{1)\ \text{Citrate},\ 2)\ \text{BSPP}} Ag_n^0 \qquad \text{(BSPP First)} \qquad (5)$$

$$n\,Ag^+ \xrightarrow[3)\ \text{BSPP}]{1)\ \text{Citrate},\ 2)\ BH_4^-} Ag_n^0 \qquad \text{(BSPP Last)} \qquad (6)$$

The experimental protocol varied addition order as well as reagent concentrations (Table 1)

Table 1: Protocol at various addition orders and reagent concentrations

Standard Order	[Citrate], μM	[$BH4^-$], μM	[BSPP], μM	Addition Order
1	400	200	50	BSPP First
2	200	400	50	BSPP First
3	200	200	100	BSPP First
4	400	400	100	BSPP First
5	400	200	50	BSPP First
6	200	400	50	BSPP First
7	200	200	100	BSPP First
8	400	400	100	BSPP First
9	200	200	50	BSPP Last
10	400	400	50	BSPP Last
11	400	200	100	BSPP Last
12	200	400	100	BSPP Last
13	200	200	50	BSPP Last
14	400	400	50	BSPP Last
15	400	200	100	BSPP Last
16	200	400	100	BSPP Last

See section 3.2 for results and discussion.

2.3.2 Investigating the Affect of Chemical Variables for Photochromic Shifts

A central composite experiment was conducted to determine which reagents were important for photochromic band shifts. In this experiment, there were five levels of silver concentrations (24, 35, 50, 65 and 75 μM), five levels of BSPP concentrations (33, 40, 50, 60 and 66 μM), five levels of BH_4^- (131, 200, 300, 400, 468 μM), and one level of citrate (200 μM) (Table 2).

Table 2: Design for chemical importance experiment

Ag (μM)	$BH4^-$ (μM)	BSPP (μM)	Citrate (μM)
24	300	50	200
35	200	40	200
35	400	40	200
35	200	60	200
35	400	60	200
50	131	50	200
50	468	50	200
50	300	33	200
50	300	66	200
50	300	50	200
50	300	50	200
65	200	40	200
65	400	40	200
65	200	60	200
65	400	60	200
75	300	50	200

See section 3.3 for results and discussion.

2.3.3 Determining Time Limitations on Synthesis of Developing Photochromic Particles

Additionally, these solutions described in Table 2 were allowed to photodevelop for a total of 240 hrs. aliquots of 24, 72 and 240 hr photodeveloped solutions were placed in the dark for 24hrs and UV-visible spectra were obtained. The differences in $\Delta\lambda$ were compared to determine if photodevelopment time was another major factor. See section 3.4 for results and discussion.

2.3.4 Testing the Limited Number of Cycles for Photochromic Ag Nanoparticle

Experiments to change the morphology of photochromic Ag nanoparticles had two steps. In step 1, the light form was placed in the dark for 16 hrs to develop the dark form. In step 2, the dark form was illuminated to convert the material to light form. Within this thesis, *cycling* is the process of converting photochromic solutions from light form $_x$ to dark form $_x$ to light form $_{x+1}$. A *cycle* consists of a series of light form to dark form with the same numerical subscript. For example, light form$_1$ and dark form$_1$ are cycle$_1$, while the act of transforming light form$_1$ to dark form$_1$ to light form$_2$ is cycling with light form$_2$ being a member of cycle$_2$ (Figure 5). Note that there can be a limitless number of cycles by repeating the dark and light transformations numerous times.

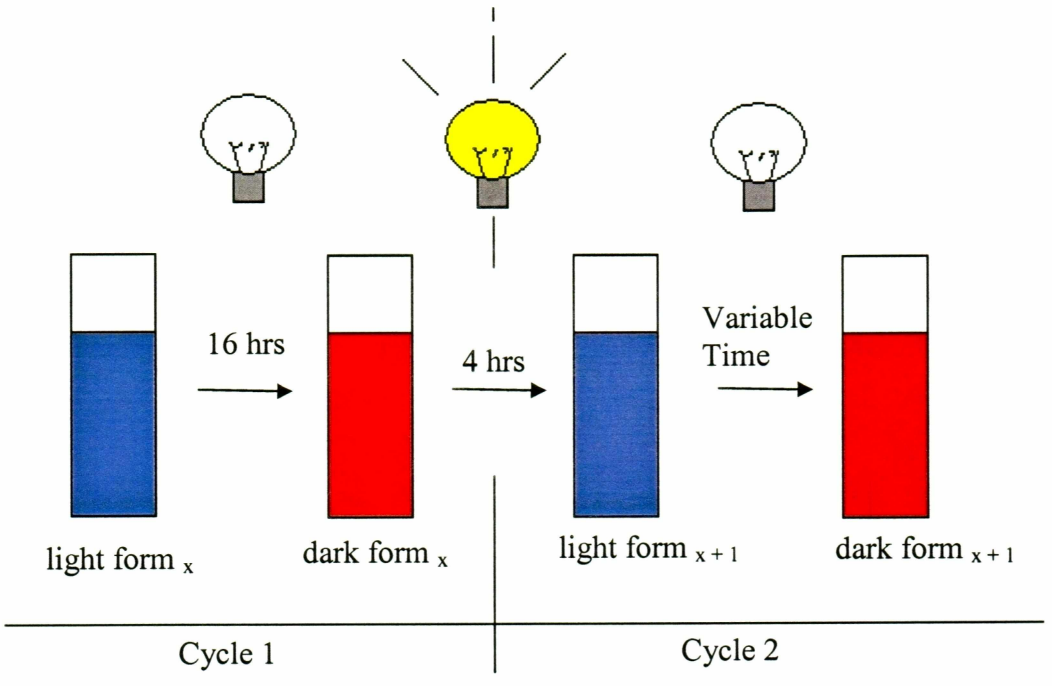

Figure 5: Clarification of cycling.

An experiment was done to determine if the spectrum of the photochromic particles would be consistent from cycle to cycle and if the nanoparticles could be cycled

many times without losing the effect. Photodeveloped solutions described in section 2.2 steps 1-5 were used. A UV-vis kinetics run was done (2.1.4.1) as the solution transformed into the dark species (section 2.2 step 6). Once the solution had completely changed into the dark form another kinetics run was done immediately during a 5hr illumination with full spectrum bulbs. The solution was cycled three more times with 24 hrs of dark and 5 hours of light exposure (producing a $cycle_4$ dark form particle). Finally, The $cycle_4$ light form was placed in the dark for 48 hrs and spectra were obtained. See 3.5 for results and discussion.

2.3.5 Testing the Effect of Filtered Light on Dark Form Photochromic Nanoparticles

An experiment was conducted to determine if filtered light would affect dark form particles differently than unfiltered light. A dark form solution was prepared (2.2). Aliquots of the solution were illuminated with filtered light (2.1.3) and UV-visible spectra were obtained. See 3.6 for results and discussion.

For this experiment sample holders were constructed to filter light between the bulbs and samples. Styrofoam boxes used to ship plastic cuvettes worked ideally for this task. A platform to hold the light filter was made by carving 1 inch by 1 inch squares out of the top of the container (Figure 6). Filters were affixed above the holes with tape. Cuvettes containing dark form solutions were placed in the center of the container and the top was taped onto the container. The container was placed under the lights. The solutions were illuminated for 5hrs.

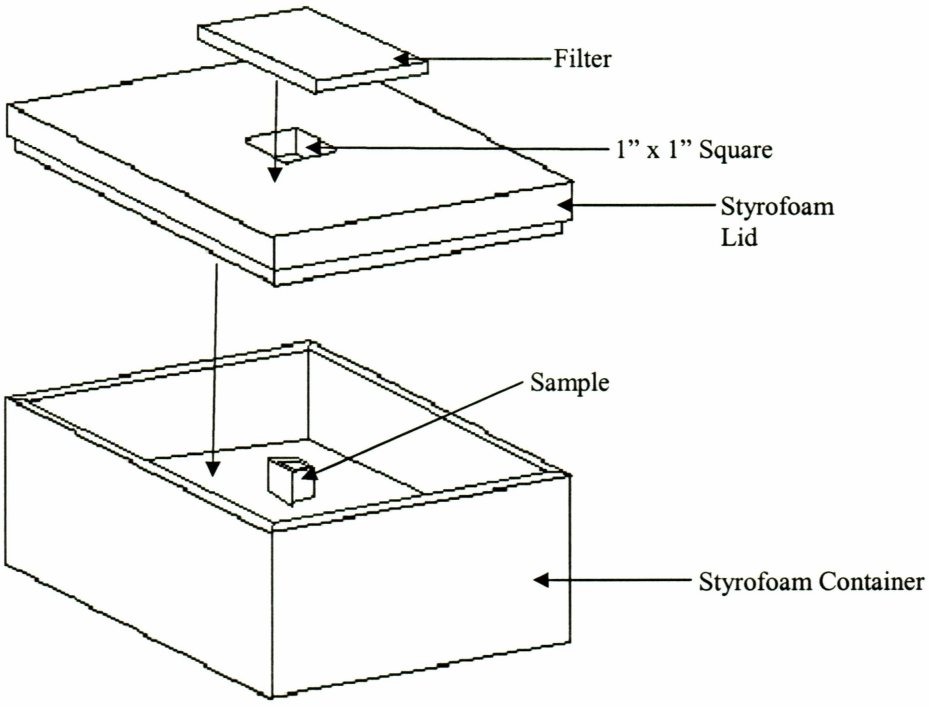

Figure 6: Sample holder diagram

2.3.6 TEM Imaging Experiment

Samples were prepared by delivering a 6 μL volume of a photodeveloped, dark form and light form Ag nanoparticle solution (2.2) by a micropipette onto a carbon type-B 300 mesh copper grid (Ted Pella, Inc.). The drop was allowed to air dry in a fume hood for 4 hrs. UV-visible spectra (2.1.4.1) and particle size (2.1.4.2) were obtained of the solution during the sample preparation. See 3.7 for results and discussion.

Chapter 3.0

Results and Discussion

3.1 Photochromic Properties

We have discovered that the shape of some Ag nanoparticles can be repeatedly changed by subjecting them to a repeated cycle of light and dark. To our knowledge, this has never been reported in the literature. The electronic spectrum (Figure 7) and color of these nanoparticles (Figure 8) changed colors dramatically because of an obvious transformation in shape of the nanoparticles (Figures 8).

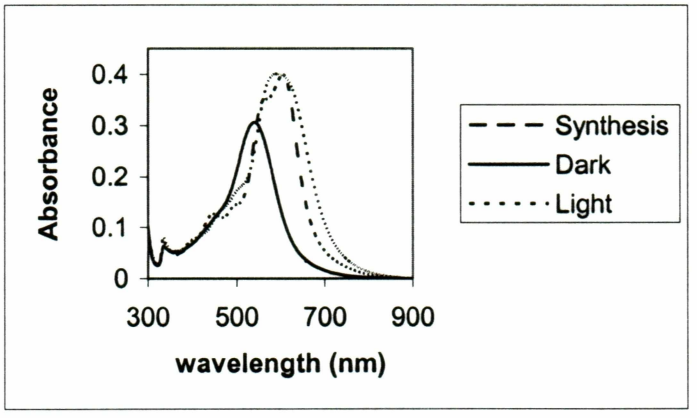

Figure 7: Absorbance spectra of Ag nanoparticles shown in Figure 8.

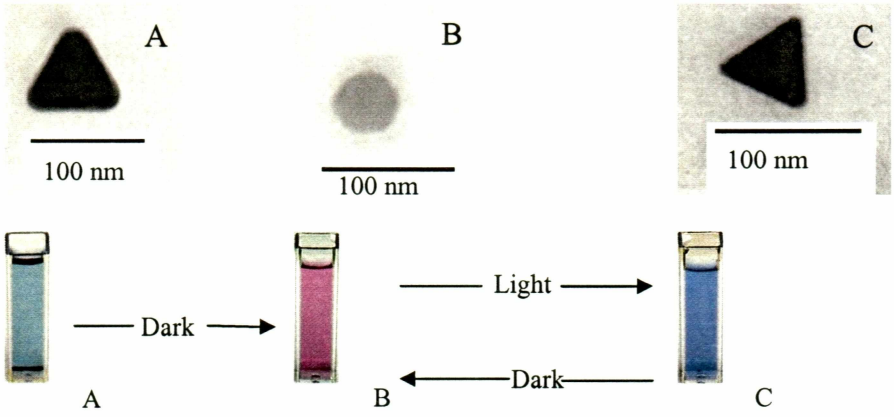

Figure 8: TEM images and photographs of photochromic silver. A) Ag nanoparticles synthesized with 24 hr illumination B) then placed in the dark for 24 hrs, C) then illuminated for 5 hrs.

3.2 Results and Discussion of Addition Order

The investigation done by Joshua Klynstra (2.3.1) showed the addition order of BSPP was critical for developing photochromic silver nanoparticles. The experiment showed that production of photochromic nanoparticles could only be achieved by addition of BSPP after reduction of the Ag (BSPP Last (2.3.1)) (Figure 9).

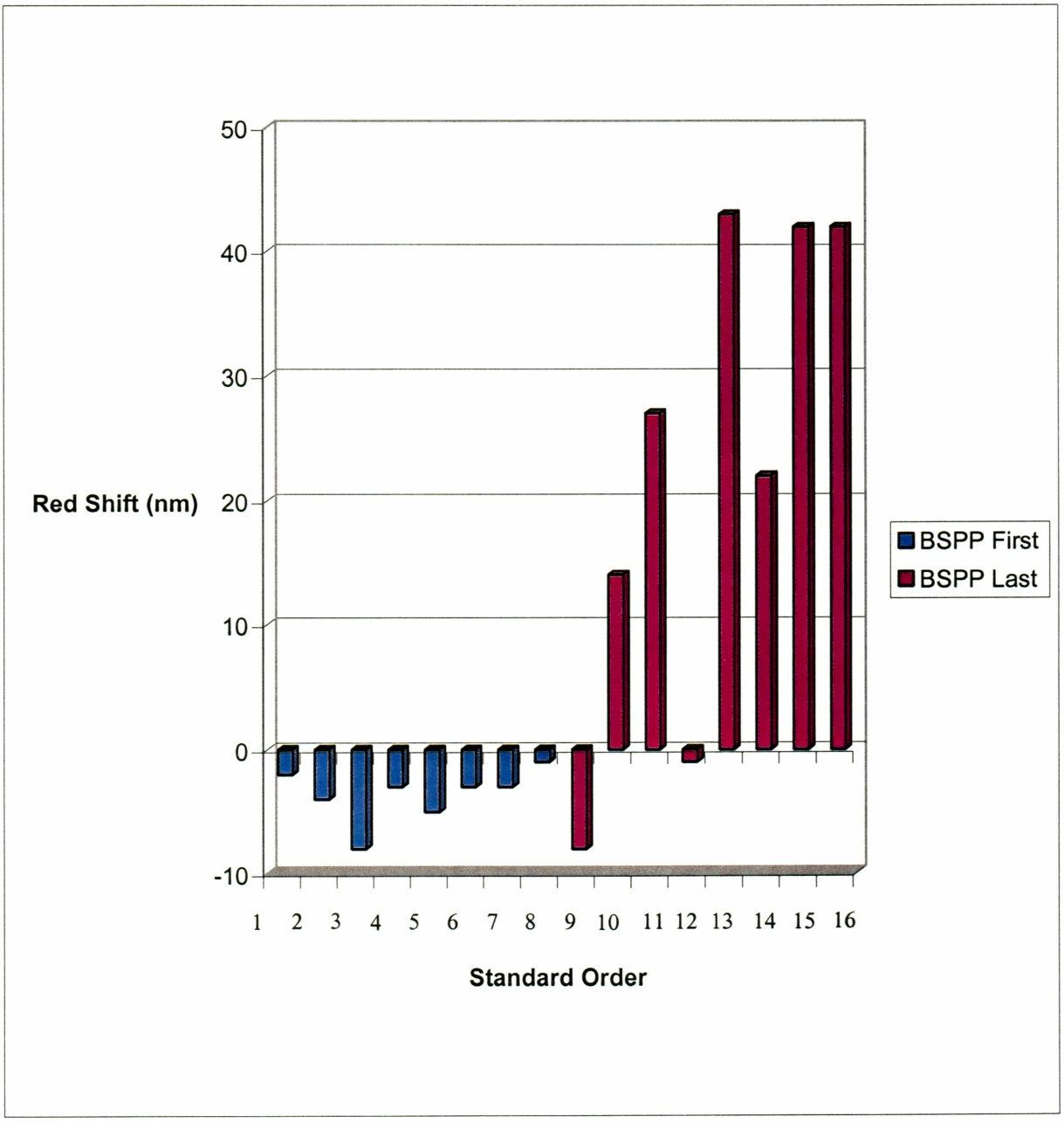

Figure 9: Results from addition order experiment from Table 1.

3.3 Results and Discussion for Chemical Importance

Ag and BSSP concentrations were the most important chemical variables that determined the size of red shift. By varying the concentration of the reagents (2.3.2) all except three of the solutions were photochromic (Figure 10).

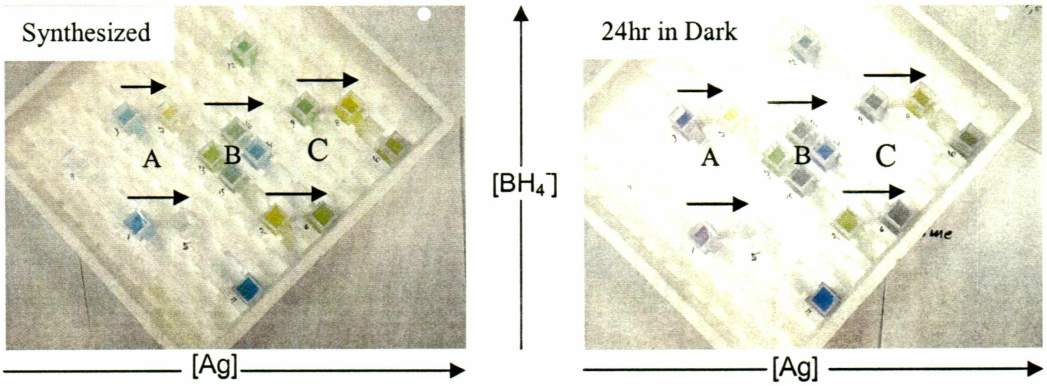

Figure 10: Photographs of initially synthesized solutions and 24 hrs in dark. The concentrations of Ag increase from left to right, BH_4^- increases from bottom to top, and concentrations of BSPP increase within groupings A, B, and C from left to right.

The numerical values of difference in bands between the light and dark form is shown in Figure 11.

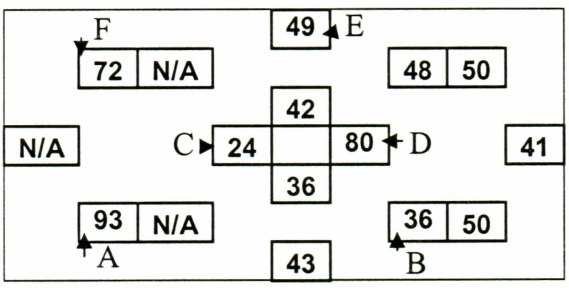

Figure 11: Numerical red shift results for change in band shifts. Boxes represent the cuvette positions as shown in Figure 9.

A variation of photochromic shift was observed according to the concentrations of chemical reagents.

The experimental results showed a 93 nm band shift for a low concentration of Ag (35 μM), while a high concentration of silver (65 μM) produced a 50 nm band shift at the 660nm band (Figure 12, 13).

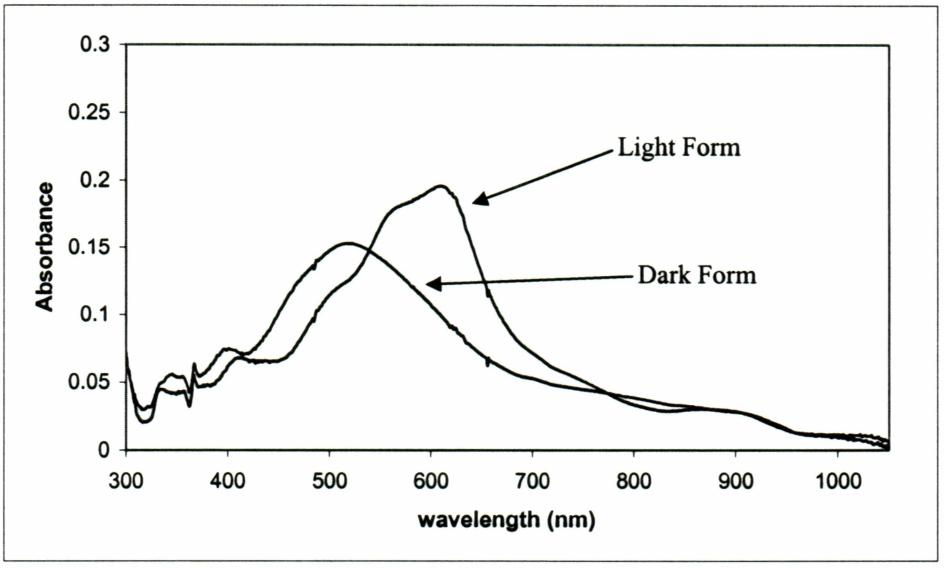

Figure 12: Low concentration of Ag produced a large red shift. Spectra of sample from Table 2 (concentrations Ag [35 μM], BSPP [40 μM], BH_4^- [200 μM]), Citrate [200 μM]). Position is represented as A on Figure 11.

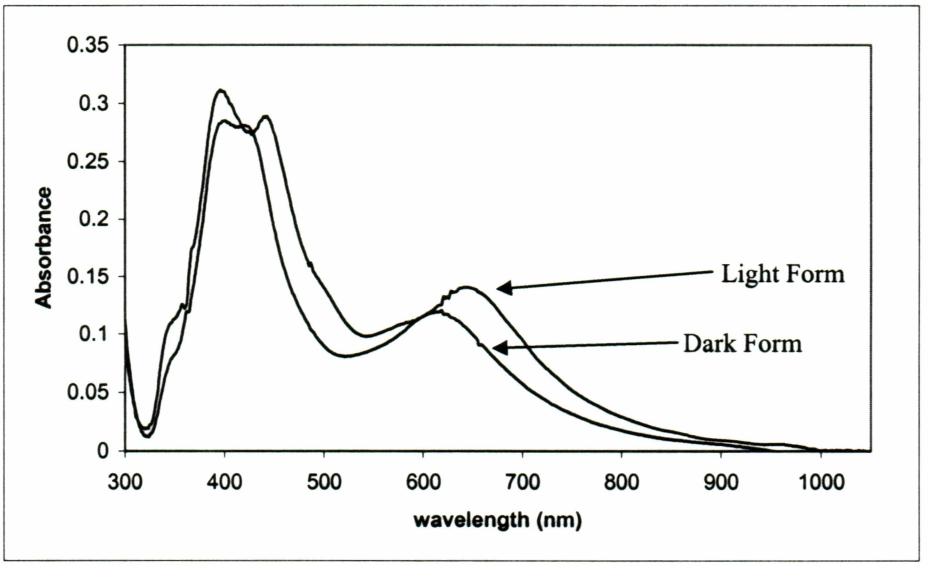

Figure 13: High concentration of Ag produced a small red shift. Spectra of sample from Table 2 (concentrations Ag [65 μM], BSPP [40 μM], BH_4^- [200 μM], Citrate [200 μM])). Position is represented as B on Figure 11.

BSPP also affected photochromic band shifts. Low concentration of BSPP (33 μM) produced a 24 nm band shift, while a high concentration of BSPP (66 μM) with all other concentrations of reactants considered equal produced an 80 nm band shift (Figure 14, 15).

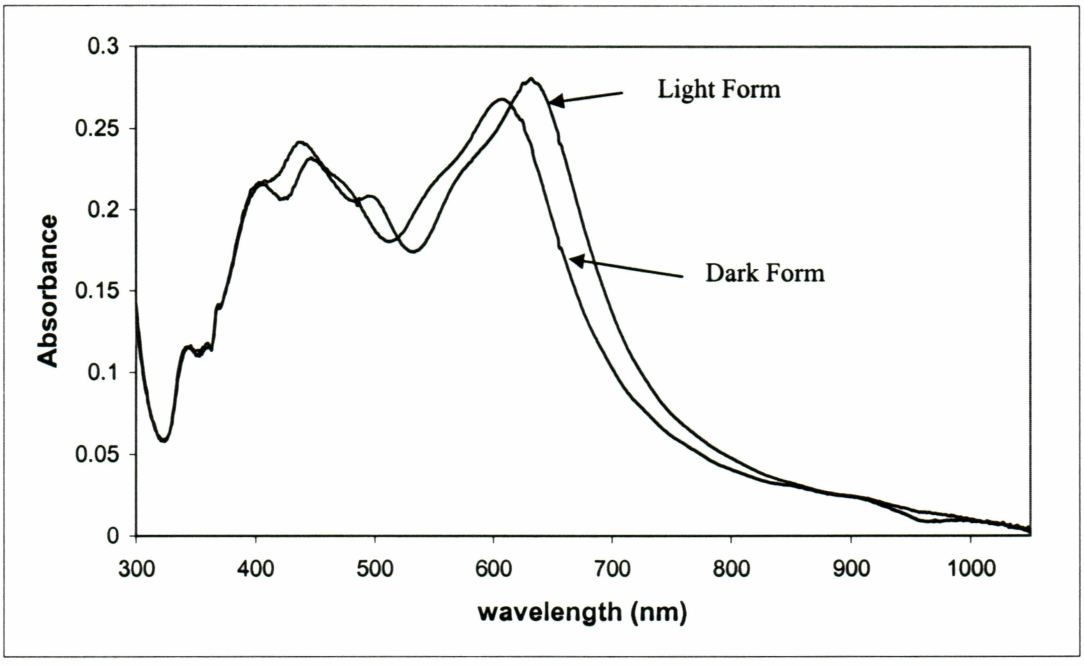

Figure 14: Low concentration of BSPP produced a small red shift. Spectra of sample from Table 2 (concentrations Ag [50 μM], BSPP [33 μM], BH_4^- [300 μM], Citrate [200 μM])). Position is represented as C on Figure 11.

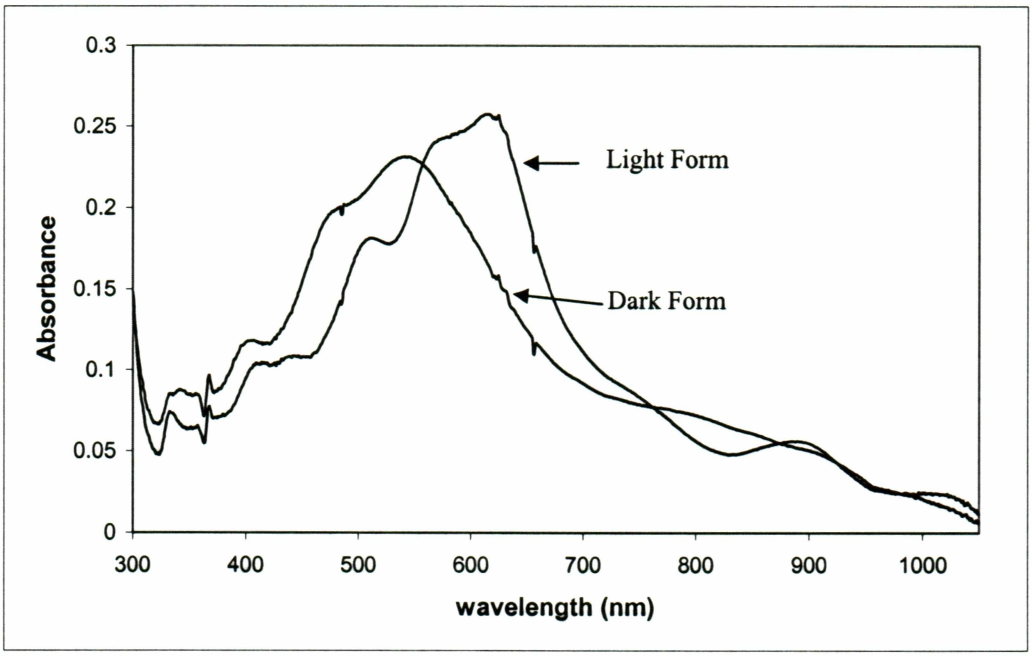

Figure 15: High concentration of BSPP had a large red shift. Spectra of sample from Table 2 (concentrations Ag [50 μM], BSPP [66 μM], BH_4^- [300 μM], Citrate [200 μM]). Position is represented as D on Figure 11.

The ratio of BSPP to Ag was examined to determine if these molar ratios were important variables. Examination of BSPP to Ag ratio showed solutions with a ratio of < 1.0 produced a small band shift; a 0.6 ratio had a 36 nm band shift (Figure 16), while solutions containing a ratio of ≥1.0 produced a large band shift. A 1.14 ratio of BSPP to Ag produced a 93 nm band shift (Figure 17). Although an increase of ratio BSPP to Ag increased the band shift, solutions with a ratio of ≥1.7 produced no band shift because the solutions color would change from an initial reduced Ag yellow color to colorless early in the photodevelopment process preventing acquisition of spectral data.

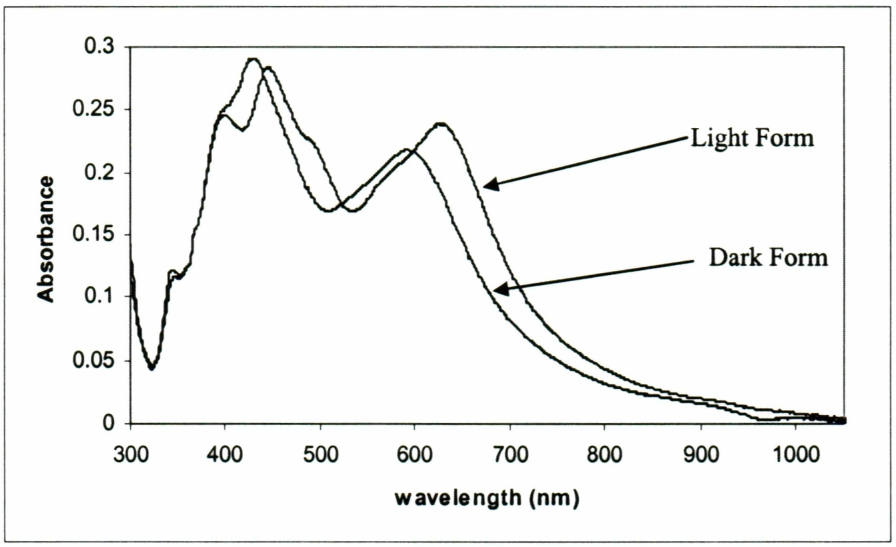

Figure 16: A 0.6 Ratio of BSPP to Ag produced a small red shift. Spectra of sample from Table 3 (concentrations Ag [65 μM], BSPP [40 μM], BH_4^- [200 μM], Citrate [200 μM]). Position is represented as E on Figure 11.

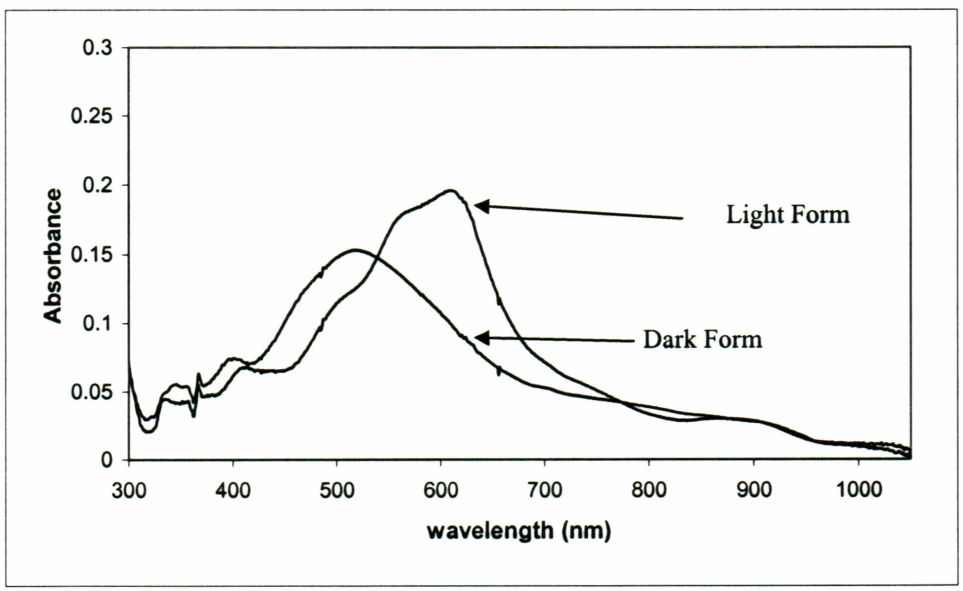

Figure 17: A 1.14 ratio of BSPP to Ag produced a large red shift. Spectra of sample from Table 3 (concentrations Ag [35 μM], BSPP [40 μM], BH_4^- [200 μM], Citrate [200 μM]). Position is represented as F on Figure 11.

3.4 Results and Discussion for Synthesis Times

The photochromic effect was observable from solutions that were photodeveloped for 24 – 72 hrs. However, no shift was observed from that were photodeveloped for 240 hr nanoparticles. The nanoparticles within the solution from this experiment (2.3.3) were photochromic after 24 hrs of photodevelopment. The 72 hr photodeveloped nanoparticles blue shifted further than the 24 hr counterpart. After 240 hrs, the nanoparticles within the solution had lost the capability to shift (Figure 18, Table 3).

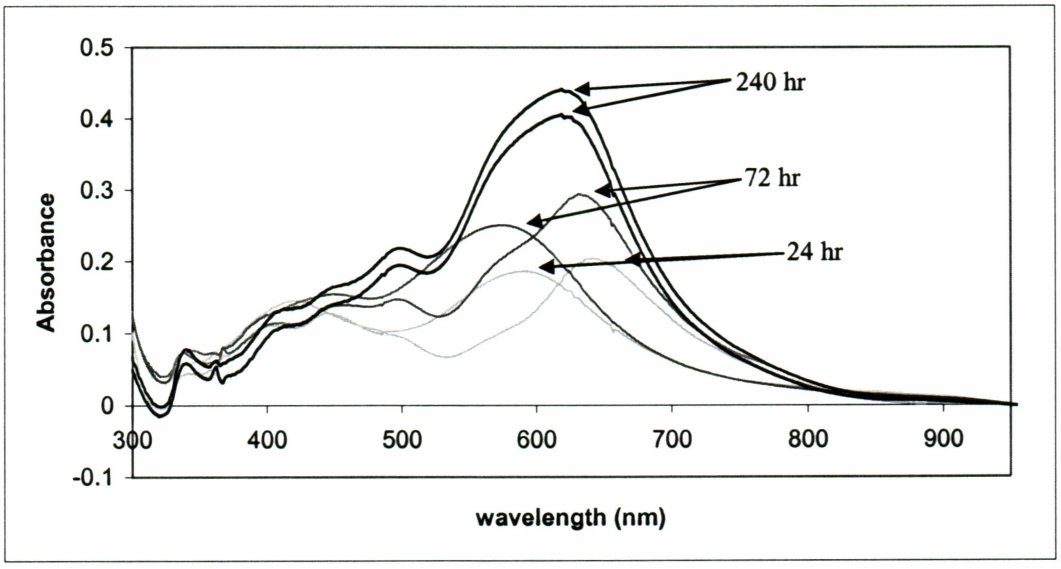

Figure 18: Spectra of light and dark forms as a function of time of illumination prior to the first dark period.

Table 3: Band shift as a function of time

Time (hrs)	Band Shift (nm)
24	50
72	60
240	0

3.5 Results and Discussion for Photochromic Shifting

UV-visible spectral features blue shifted from synthesized to dark form. The blue shifted of 60 nm was complete within 16 hrs (Figure 19). The band maximum remained at 560 nm after 16 hrs in the dark suggesting that the transformation was complete.

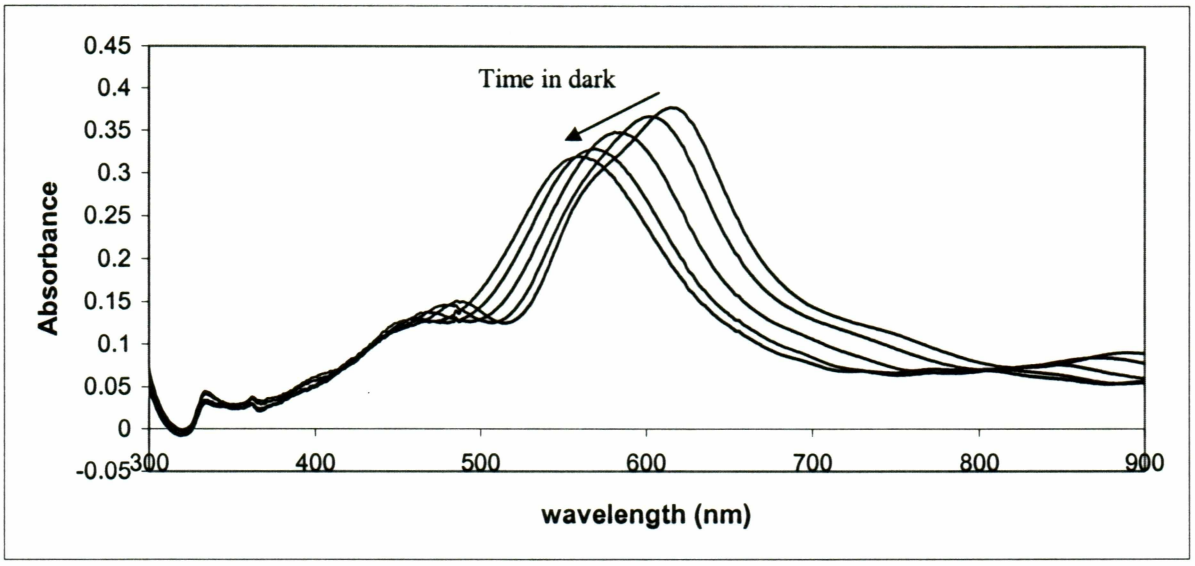

Figure 19: Spectra of photochromic solution from synthesis (24 hr light synthesis) to dark form (16 hrs dark). Displayed spectra are in multiples of 4 hrs with the far right band corresponding to 0 hrs and the far left band corresponding to 16 hrs.

The transformation of the Ag nanoparticles and the resulting spectrum was four times as rapid when the dark form was illuminated (Figure 20). Formation of the light form completed in four hours. The transformation was a result of light source and emission wavelength and it will be affected differently by specific transmitted wavelengths and conditions (3.6). The final spectrum compared to that of the originally photosynthesized particles. Although this reaction would be expected to be a zero order rate, no rate order could be determined.

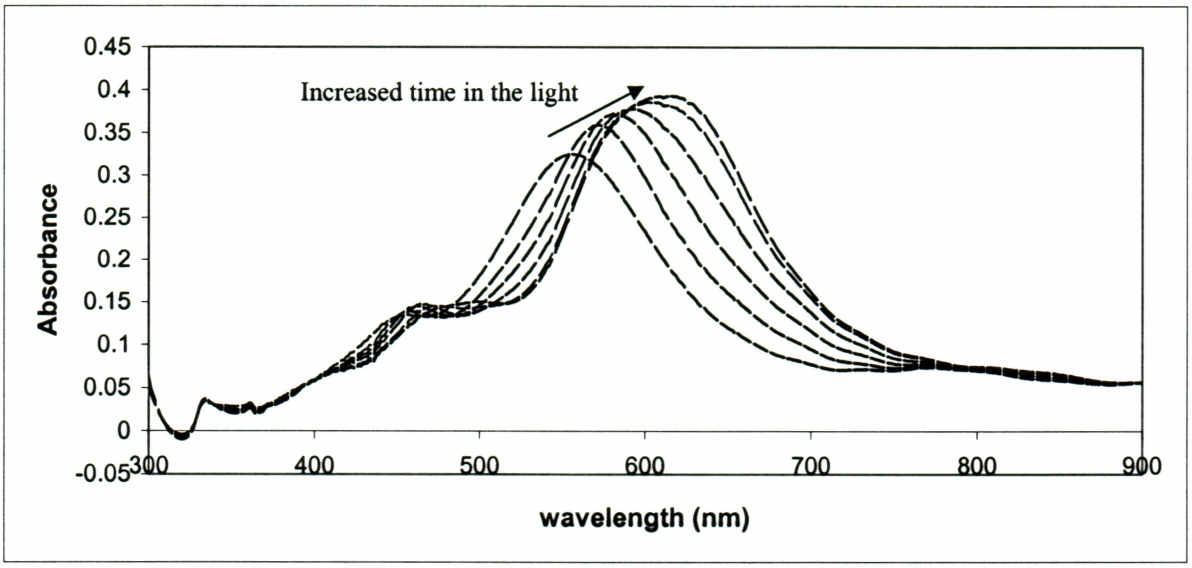

Figure 20: Spectra of photochromic Ag from dark form to 4 hr illumination. Times are from left to right are 0, 0.5, 1, 2, 3, and 4 Hrs.

The transformation from dark to light form rate order could not be determined.

Freshly prepared photochromic particles were cycled between the light and dark forms several times by placing the dark form into the light for 5 hrs to produce light form particles. Light form particles were placed into the dark for 24 hrs to make dark form particles. Particles did not blue shift as far between dark cycles, while light form bands generally ended at 640 nm (Figure 21, Table 4). It thus appears that the photochromic particles may be cycled a limited number of times.

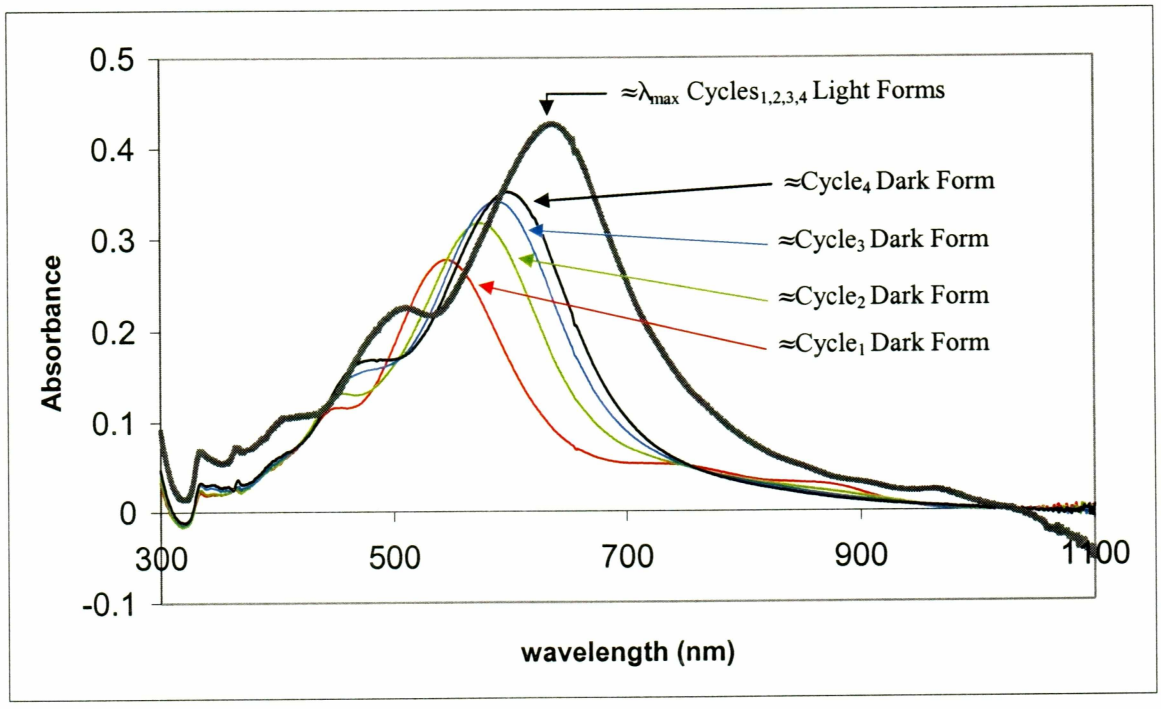

Figure 21: Light and dark spectra for four cycles. $Cycle_1$ (red), $Cycle_2$ (green), $Cycle_3$ (blue), $Cycle_4$ (black) Average baseline correction at 1050nm.

Table 4: Comparison of band shift between cycles

Cycle #	Light Form Band Maximum	Dark Form Band Maximum	Δλ (nm)
Cycle 1	635	553	82
Cycle 2	637	580	57
Cycle 3	636	593	43
Cycle 4	640	600	40

It turned out that not much change occurred in the spectra of the $cycle_4$ dark form solution that was placed in the dark for 48 hrs (Figure 22). An isobestic point became apparent between the three spectra (light $form_4$, dark $form_4$, and 48hr old dark $form_4$) at 540 nm as the spectral profile increased as a function of time in the dark. This strongly suggests that two forms exist between the light and dark form of the solutions.

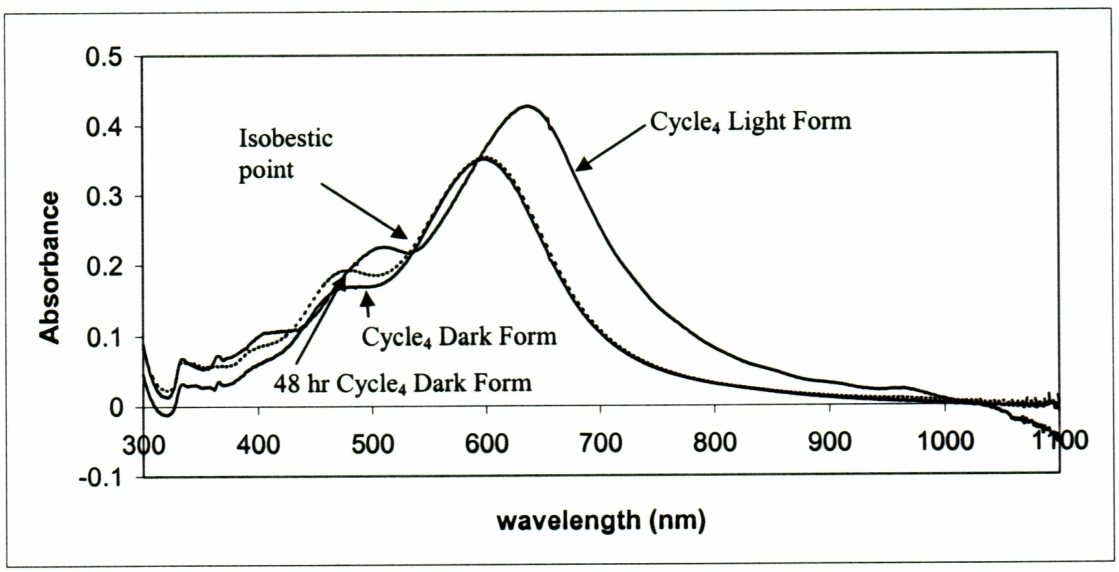

Figure 22: Comparison of dark form spectral features. The dotted spectrum was taken 24 hrs after the corresponding overlaid solid spectrum. Average baseline correction 1050 nm.

3.6 Results and Discussion for Filtered Light

When four different light filters from section 2.1.3 (Figure 2, Figure 3) were used with the lamp profiled in 2.1.3 (Figure 1) to transform the dark form of silver nanoparticle to light form, four different spectra were observed after 4 hrs of illumination (Figure 23).

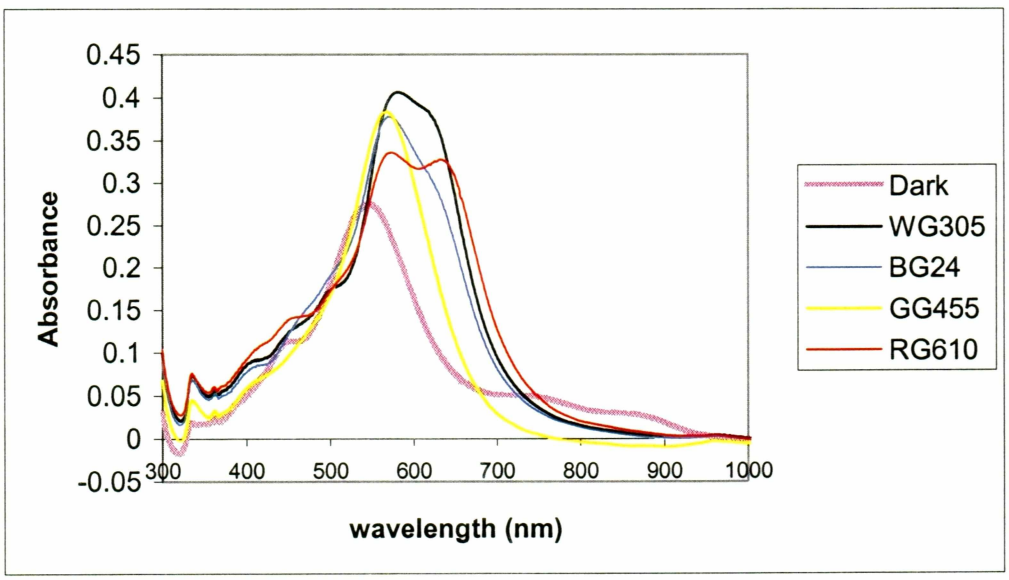

Figure 23: UV-visible transformation results of a photochromic solution from filtered light. The WG-305, BG-24, GG-455 and RG-610 filters were used in this experiment.

Specific transmitted wavelengths are likely responsible for the photochromic shifts because band shapes and shifts varied depending on filtered light. If the photochromic transformation was not dependent on specific spectrum of excitation source of emitted light, then equal band shapes and shifts would be expected amongst the four solutions. The WG-305, which filtered the least amount of visible light, had the largest overall spectral profile. The RG-610 filter had about the same band shift as WG-305, but had a very different spectral profile. BG-24 had considerably less band shift than RG-610, and GG-455 had an even smaller band shift than BG-24.

3.7 Results and Discussion from Transmission Electron Microscope Imaging

TEM images (2.3.3) showed different shapes between photodeveloped, dark, and light form. These Ag nanoparticles were photochromic with $\Delta\lambda \approx 70$ nm.

The TEM images showed that synthesized Ag nanoparticles with photochromic properties have trigonal plate structures with sizes ranging from 30 to 80 nm (Figure 24). The thickness is approximately 12 nm (Figure 25).

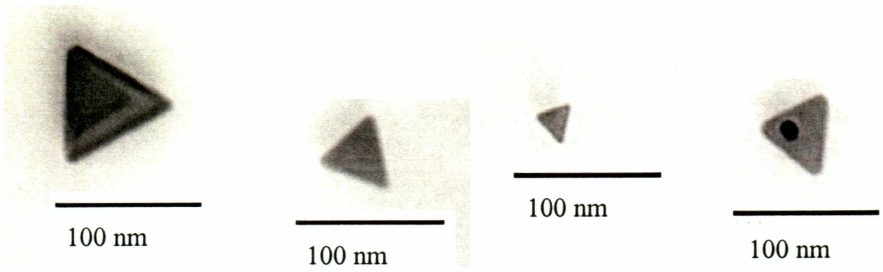

Figure 24: Lateral TEM images of photodeveloped Ag nanoparticles.

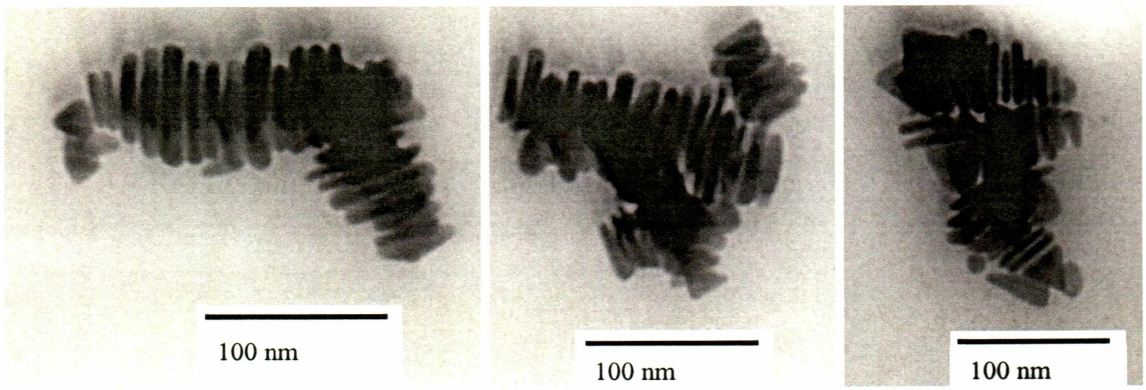

Figure 25: Vertical TEM images of photodeveloped Ag nanoparticles.

The images of the dark form particles are circular discs or highly rounded triangular discs with size from 25 nm to 80 nm (Figure 26). These particles are aggregated to a lesser degree than the initially synthesized particles. The thickness is similar to the photodeveloped particles (Figure 27)

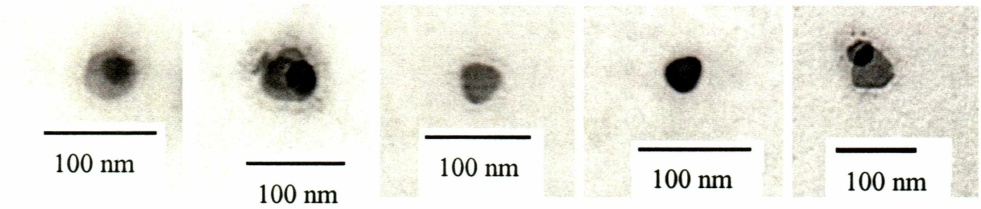

Figure 26: Lateral TEM images of dark form Ag nanoparticles.

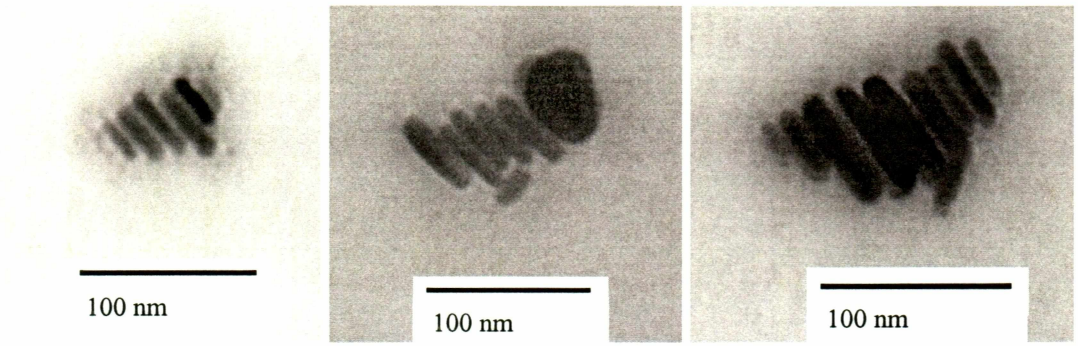

Figure 27: Vertical TEM images of dark form Ag nanoparticles.

The images of the light form show that the nanoparticles approach the trigonal profile of the originally synthesized particles after 4 hrs of illumination (Figure 28 and 29).

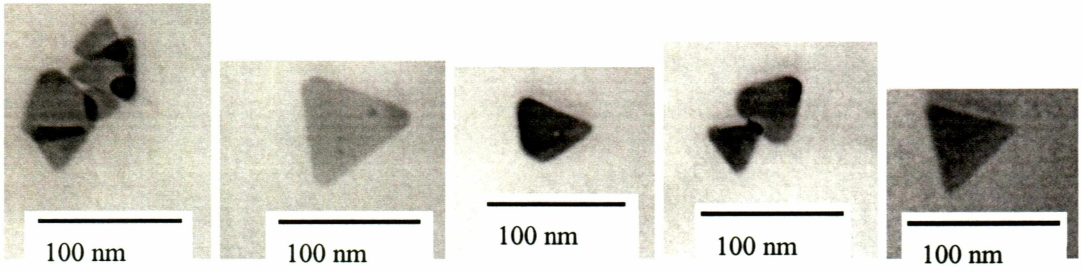

Figure 28: Lateral TEM images of light form Ag nanoparticles.

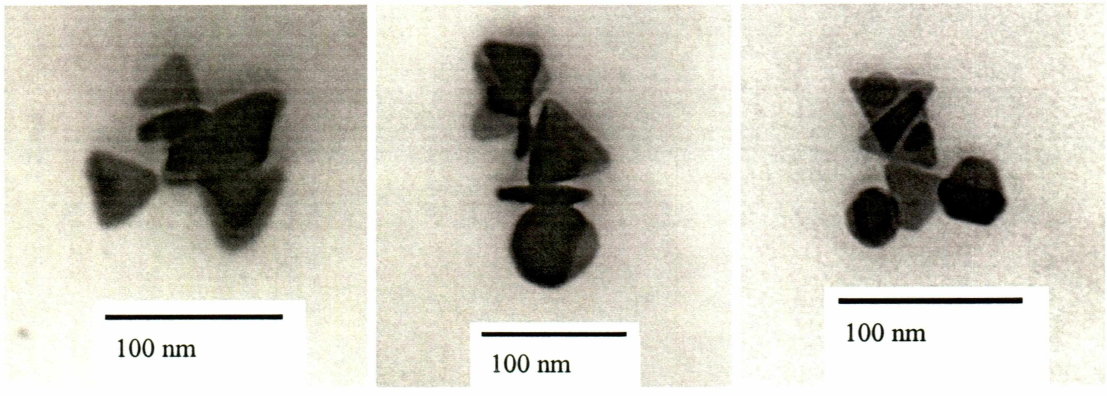

Figure 29: Vertical TEM images of light form Ag nanoparticles.

Polygon structures became evident within the light form images. These structures were not in photodeveloped nor dark form images. The structures are probably truncated nanostructures that formed in the dark species, but were unable to sharpen (Figure 30).

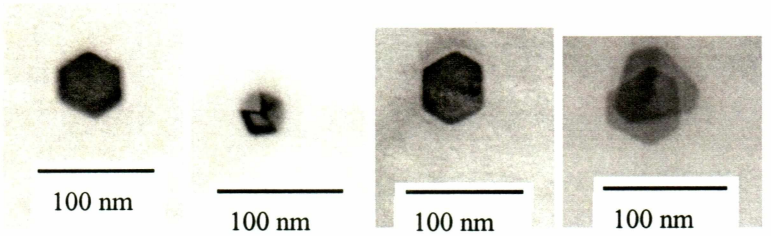

Figure 30: Different morphologies of light form nanoparticle.

Some difference occurred in the spectral bandwidths of the two light forms (Figure 31).

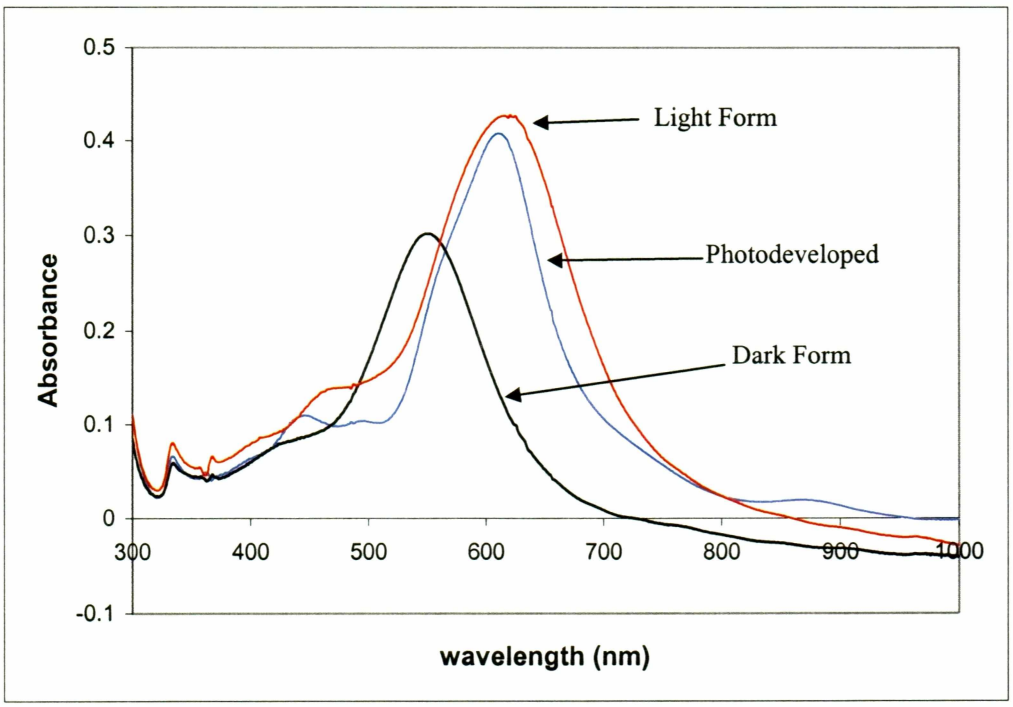

Figure 31: Photodeveloped, dark form, and light form spectra of solutions used for TEM imaging.

Chapter 4.0

Conclusion

Pure chemically homogenous photochromic nanoparticles, which develop by photoinduced self-assembly without supports, could yield tremendous potential in the realm of nanochemistry and nanotechnology. These particles are highly controllable once photochemically synthesized. Furthermore, the synthesis of these particles occurs with little effort and a high percent yield of photochromic behavior observed.

Reagents for chemical synthesis were highly significant. All four chemical reagents used in this experiment were required to produce the photochromic solutions. In addition, cleanliness of glassware and water were imperative to making photochromic solutions.. Although all chemicals were important for photodevelopment, it seems clear that Ag and BSPP were the two major contributors to band shifts. Low concentrations of Ag and high concentrations of BSPP produced large spectral shifts.

Although individual solutions changed form differently, as evidenced within the UV-visible spectral profiles, the solutions all portrayed common behavior. All photochromic solutions blue shifted when placed in the dark and red shifted when placed in the light. The solutions took 16 hrs to completely change to the dark form from photodevelopment and approximately 4hrs to completely change to the light form from the dark form. Photochromic solutions could be cycled between light and dark forms. However upon completion of cycling, the solutions lose the capacity to blue shift to a certain extent.

The Ag photochromic particles investigated displayed at least two considerably different states indicative of the form of the solution (dark and light) which were ultimately controlled by particle shape. Photodeveloped particles had prismatic configurations, dark form particles truncated (rounded), and light form particles transformed shape back to prismatic. The difference in state could be visually determined by the color of the solution. These solutions can be photochemically developed within 24hrs and converted into dark form by placing them in the dark for 14hrs. This means that these particles could be made in a timely manner at low cost and with considerable ease.

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